

Design and Characterization of an Ultrafine Coal Ash Aerosol Generator for Direct Animal Exposure Studies

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ABSTRACT

Primary ultrafine particulate matter (PM) is produced during pulverized coal combustion by the nucleation and heterogeneous condensation of vapor-phase species. This differs from the mechanisms that control the formation of the supermicron fly ash that is heavily influenced by the fragmentation and coalescence of aluminosilicate phases derived from clay minerals in the coal. Although the ultrafine fraction typically represents much less than 1% of the total fly ash mass, this fraction dominates the particle number concentrations and exhibits reduced collection efficiency through particulate control systems.

Exposure studies for health effect assessments are performed typically by intratracheal instillation of collected particles that does not necessarily simulate actual mechanisms of pulmonary exposure. This paper describes the design and characterization of an ultrafine coal ash generator that can be used for direct animal inhalation exposure studies. The system consists of a pulverized coal feeder, an externally heated three-zone drop tube furnace, a cyclone particle separator, and an exposure chamber. Utah and Illinois bituminous coals have been characterized in preparation for animal exposure studies. In addition to temperature, pressure, humidity, noise, and gas concentrations (O₂, CO₂, CO, NO, and SO₂), the chamber environment has been characterized for ultrafine particle mass, particle number, and particle size distribution. Extracted PM samples have been characterized by scanning electron microscopy and X-ray fluorescence spectroscopy. The system as currently configured is capable of conducting acute and chronic studies and is able to operate continuously up to 12 hours with minimal supervision.

Keywords: ultrafine, coal ash, drop tube furnace, direct exposure

INTRODUCTION

Ultrafine particles, often defined as those less than 0.1 micrometers (μm) in aerodynamic diameter, are generated during combustion of coal and other fuels by the nucleation, heterogeneous condensation, and coagulation of vapor phase organic and inorganic matter associated with the fuel. These particles are often enriched in various semi-volatile elements including a number of toxic metals, and grow via coagulation and agglomeration processes to produce an accumulation mode aerosol with diameters typically between 0.1 and 0.5 μm . In contrast, combustion generated particles greater than 1 μm are typically the result of fragmentation and coalescence of non-volatile mineral macerals. As a result, combustion generated submicron and supermicron particles often have very different physical and chemical characteristics^{1,2}. A recent study also suggests that accumulation mode coal fly ash can elicit a greater toxic response compared to coarse mode fly ash³. Although ultrafine coal fly ash particles typically constitute less than 1% of the total fly ash (by weight), their number concentrations are very much higher. In addition, their small size makes them difficult to control and promotes their inhalation and penetration deep into the respiratory tract.

Several aerosol sampling systems have been developed to perform direct particle exposure experiments. Gordon et al.⁴ developed an ambient aerosol concentrator capable of conditioning and delivering particles as small as 0.5 μm (mass mean diameter) at concentrations up to 10-times ambient. Schermuly et al.⁵ nebulized surfactant to generate aerosols with mass median diameter of 4.5 μm . They concluded that low doses of ultrasonically delivered natural surfactant are as effective as 'conventional' doses of intratracheal instilled surfactant, but had advantageous effects with regard to lung ventilation and perfusion. Vlasenko et al.⁶ developed a dust disperser using a standard PM (Arizona road dust) within the size range 30–1000 nm for heterogeneous reaction studies in flow reactors. They found that particles larger than 100–200 nm shrank about 1% once exposed to relative humidity >90%. This was interpreted as being due to the restructuring of the larger dust agglomerates to particles with smaller mobility diameters due to the effect of water vapor. Seagrave et al.⁷ investigated and compared the health effects of gasoline and diesel engine exhaust PM containing volatile compounds using both in-vivo and in-vitro techniques. Fernandez et al.⁸ studied the health effects of fine particles from coal and refuse derived fuel combustion, which were generated by re-suspension with the mean size of 2 μm .

In developing a PM inhalation exposure apparatus, one must consider many factors including the PM size and concentration, concentrations of possible gas phase co-pollutants (CO, NO, NO₂, SO₂, etc.), chamber flow rates and residence times, oxygen concentrations, temperature, humidity, and noise. Pauluhn⁹ reviewed various inhalation exposure techniques, and recommended the use of single agent systems to assess health effects. However, while this

approach avoids issues associated with evaluating and separating individual contributions from complex mixtures, it does not allow direct exposures to actual combustion particle emissions.

In addition to direct exposure approaches, a number of indirect techniques are available. Fernandez et al.⁸, for example, used a brush feeder to re-entrain collected coal and sewage sludge fly ash particles for animal exposure, and Gilmour et al.³ used instillation techniques with coal fly ash particles suspended in saline. However, neither of these approaches completely simulates real world inhalation exposures. Collected particles are often very difficult to re-entrain to reproduce the original particle size distribution, and instillation does not simulate mechanisms of exposure including aerosol fluid dynamics and lung deposition. The system described here is designed to allow direct animal exposure of combustion generated particles.

COMBUSTOR and EXPOSURE CHAMBER

System Flow and Pressure

The system schematics are shown in Figure 1. It is a closed system and designed to control each flow independently. Compressed air (>345 kPa) is used both as combustion air and by the fuel injector to entrain and transport the pulverized coal to the furnace. The combustion air and transport air are both controlled by separate flow meters. A back pressure regulator is used to maintain the slightly less than ambient pressure (~2.5-5 cm H₂O less than atmospheric) in the furnace. To maintain the required 40-60% relative humidity within the exposure chamber, the combustion air is saturated prior to its introduction to the furnace. This is accomplished by bubbling the combustion air through water maintained at 35 °C within a constant temperature bath.

Additional compressed air is used by a jet pump after the furnace to provide air for quenching and dilution of the flue gas from the furnace and also to boost the pressure within the chamber that would normally be reduced by the five stage cascade cyclone system. This approach allows the exposure chamber to operate near atmospheric pressure (~15 cm H₂O less than atmospheric).

Drop Tube Furnace

The schematics of the drop tube furnace are presented in Figure 2. The thermal energy required is provided by a Lindberg 5400 series tube furnace (Model No. 54679). This furnace has three zones that operate on 240 volts, 50/60 Hz and has a maximum temperature of 1500 °C. The furnace contains 30 silicon carbon heating elements.

Figure 1: Schematics of the Coal Ash Aerosol Generator and Animal Exposure Chamber

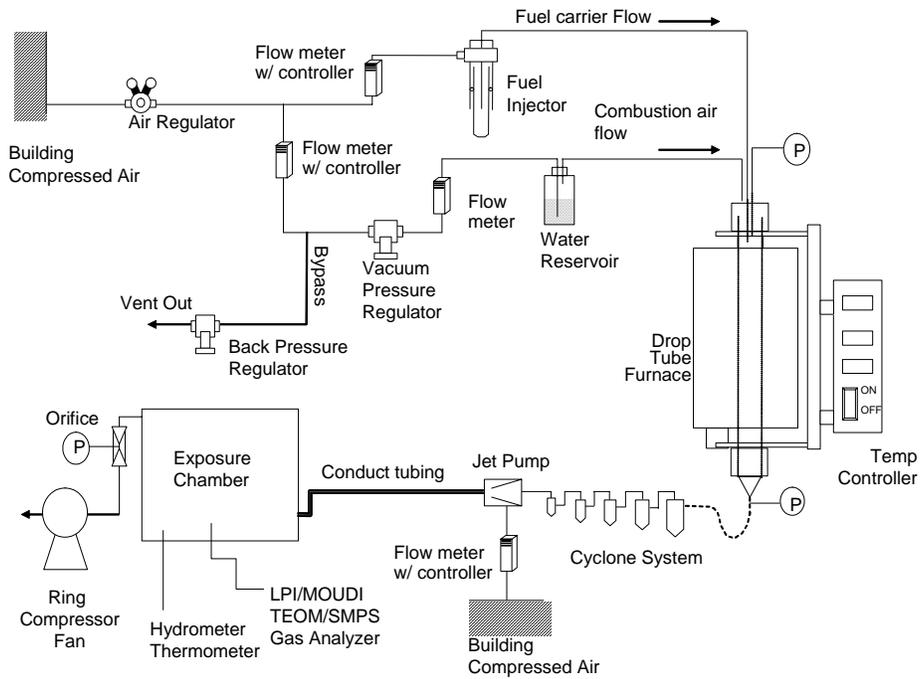
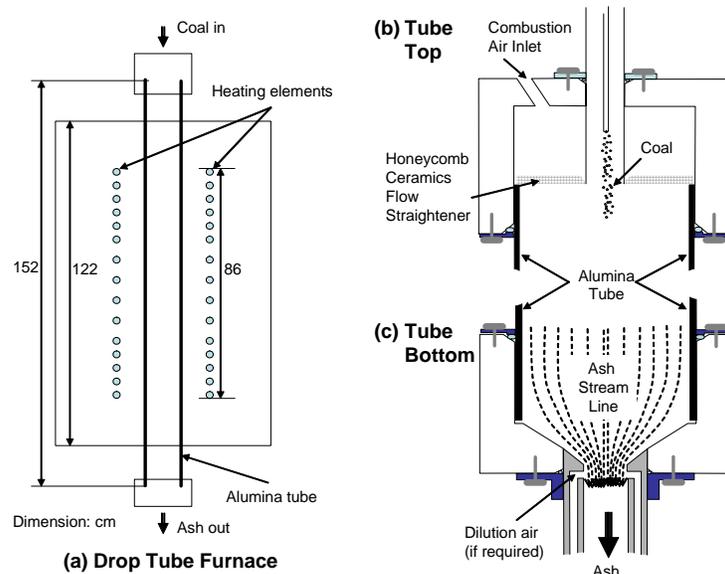


Figure 2: Schematics of the Drop Tube Furnace with Detailed Top and Bottom Sections



The heating rate, dwell time, and temperature setting for the furnace are controlled by a Eurotherm controller/programmer type 812, Part No. HA018875. To prevent thermal shock to these heating elements the furnace heating rate is held to 2.5 °C per minute until operating temperature is reached.

The pulverized coal and air are burned in a 5.1 cm inside diameter, 152 cm long alumina tube that serves as the combustion chamber contained within the vertically supported Lindberg furnace. The alumina tube is supported at the top and bottom by aluminum plates designed to flex slightly to accommodate thermal expansion. The top and bottom clearances between the alumina tube and furnace openings are packed with kaowool.

Fuel is introduced to the top and combustion products are exhausted from the bottom of the combustion chamber. The combustion air is introduced to the top of the furnace (see Figure 2b). To prevent turbulence within the combustion chamber a ceramic honeycomb flow straightener is used. The bottom of the furnace is tapered to minimize ash deposition and direct all the combustion products through the sampling probe (see Figure 2c). Furnace Reynolds number and residence time are approximately 340 and 2 s, respectively.

Coal and Injection Apparatus

Figure 3 shows the coal injection apparatus. The approach used was adapted from the device designed by Quann et al.¹⁰. The concept is that coal particles are entrained by a carrier gas (transport air), which flows over the surface of an agitated coal bed and into a stationary tube (ID 1.4 mm, depicted in Figure 3). The flow in the tube varies between 0.5 to 1.5 L/min which is sufficient to keep the particles in suspension.

The coal bed moves by means of a motorized screw syringe pump towards the stationary tube where the transport air maintains a fixed clearance. A range of stable coal feed rates are possible by varying the screw speed. The flow rate of the transport air is determined in relationship to the flow rate of combustion air so as to maintain equal velocities and laminar flow within the combustion chamber. Pneumatic or electric vibrators are utilized to agitate the coal bed surface and to keep the coal bed bulk density consistent. Additional vibrators are utilized to keep particles from deposition within the transfer tubing.

Exposure Chamber

In addition to the exposure chamber described in Figure 1, a second air-only chamber is used as a control. Each chamber operates at a flow rate of ~35 L/min which is optimized to meet the exposure requirements and limitations summarized in Table 1.

Figure 3: Schematics of Coal Injection Apparatus

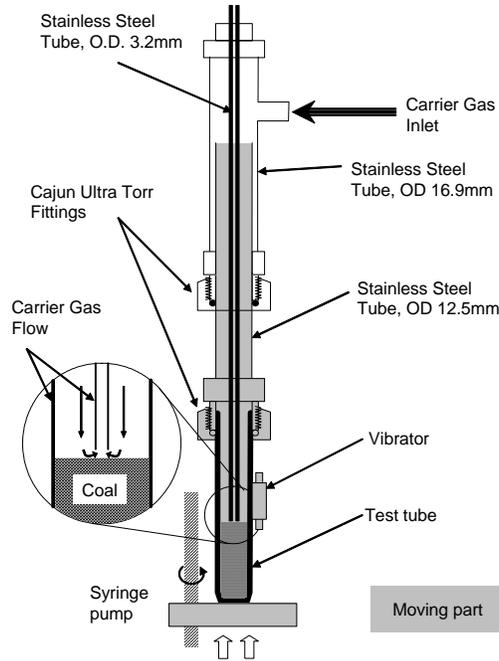


TABLE 1. Chamber Target and Actual Conditions for Animal Exposure Tests

	Chamber Target	Actual Condition	
		Utah coal	Illinois coal
Temperature, °C	20 ~ 25	21 ~ 23	21 ~ 23
Relative Humidity, %	40 ~ 60	42 ~ 44	42 ~ 44
Gas Concentration			
SO _x , ppm	< 10	0.9	7.5
NO, ppm	< 10	4.3	3.7
NO ₂ , ppm	< 1	0.35	0.27
CO, ppm	< 10	ND	ND
O ₂ , %	~ 21%	21%	21%
PM Concentration *, µg/m ³		202	406
Particle size	< 1 µm	< 1 µm	< 1 µm

* PM Concentration is based on a coal feed rate of 1.2 g/hr with 0.5 L/min of transport air

To achieve these requirements, the jet pump is used to quench and dilute the combustion products. The chamber flow and pressure is partially controlled by a ring compressor fan at the exhaust. The internal volume of chamber is 134 L, resulting in a sample exchange rate of 0.26

exchanges per minute. While this chamber was originally designed for exposure tests using gases, real-time PM measurements determined using a Thermo Electron Corp., R&P Series 1400a Tapered Element Oscillating Microbalance (TEOM) indicate that particles <1.0 μm are evenly distributed within the chamber volume.

Sampling and Monitoring of Flue Gas

From the combustion chamber, the combustion products are directed through a five stage cyclone (Thermo Electron Corp., In-Stack Cascade Cyclone Samplers). The cyclone removes the coarse mode particles with minimal pressure drop. The 50 percent particle collection efficiencies (D_{p50}) of these cyclones vary with the flue gas temperature and flow rate through the cyclones¹¹. In this study, the flow rate and temperature through the cyclone are 12.5 L/min and about 80 °C, respectively. The cyclone is heated to prevent water of combustion from condensing within the cyclone. A smaller size cut can be obtained, either by increasing the flow rate or by additional heating of the cyclone.

In addition to continuous emission monitors (CEMs) to measure chamber concentrations of a number of gas species including O₂, CO, CO₂, NO, NO₂, and SO₂, and continuous measurements of temperature, pressure, relative humidity, and noise, several instruments and measurements were used to characterize particle size distributions and mass concentrations. An MSP Inc., 10-stage, 30 L/min micro-orifice uniform deposit impactor (MOUDI) was used to segregate and collect particles as small as 0.05 μm , and these samples were used for chemical analysis by wave dispersive X-ray fluorescence (WD-XRF) spectroscopy. A TSI Inc., Scanning Mobility Particle Sizer (SMPS) was also used to measure particle number and volume distributions over the size range 0.015-0.7 μm . A TEOM was used to continuously monitor chamber PM mass concentrations. The TEOM measurements agreed with PM mass concentrations determined gravimetrically from filter samples.

Combustion of Two Different Types of Coal

The furnace and chamber system was characterized using two bituminous coals (Illinois and Utah). Table 2 presents the properties of these coals. Both have ash contents of approximately 10%. However, the sulfur contents of each coal are significantly different. Both pulverized coals had similar mean diameters (~80 μm), and the furnace flows and operating conditions were identical. These include coal feed rates of 1.2 g/hr, combustion air flow rates of 12 L/min, transport air flow rates of 0.5 L/min, and dilution air flow rates of 23 L/min. The furnace temperature was held constant at 1350 °C and the residence time through the furnace was about 2 seconds.

RESULTS and DISCUSSIONS

Figure 4 presents the CEM and the TEOM results from 14 hours of continuous operation burning Utah coal. The concentrations of gas phase species were stable and within the exposure limits identified in Table 1. The mass concentration of the submicron PM was also stable, producing submicron particle chamber concentrations of approximately 200 $\mu\text{g}/\text{m}^3$.

Particle Size Distribution and Morphologies

Figure 5 presents the number and volume particle size distributions (PSDs) and scanning electron micrograph (SEM) images of the submicron particles present in the exposure chamber during combustion of each coal. The total number concentration for the Utah coal ($6.4 \times 10^5/\text{cm}^3$) is slightly less than half of the total number concentration for the Illinois coal ($1.6 \times 10^6/\text{cm}^3$), and this translates into smaller mean particle diameters (due to slower coagulation rates), and reduced volume distributions. This is consistent with gravimetric measurements, which indicate chamber mass concentrations of 202 and 406 $\mu\text{g}/\text{m}^3$ for the Utah and Illinois coals, respectively. With regard to the Utah coal measurements made without the cyclone indicate that approximately 0.6% of the fly ash mass is partitioned to particles less than 1 μm diameter, 3.5% between 1 and 2.5 μm diameter, and 95.9% on particles larger than 2.5 μm diameter. This is consistent with previous work using a 4 kg/h laboratory-scale pulverized coal combustor equipped with a variable swirl burner and operated at a stoichiometric ratio of 1.2 that reported between 3.5 and 6.7% of the fly ash mass on particles less than 2.5 μm diameter for five coals examined².

XRF Analysis

Figure 6 presents XRF analyses results determined from total ash samples collected from the exposure chamber on polycarbonate filters. These analyses indicate that these submicron particles are composed primarily of alkaline metals (Na and K), sulfur, and iron. Carbon was not determined. The unknown values from XRF analysis were less than 5% which can be regarded as carbon. The Illinois coal ash contains notably higher sulfur content, and this is consistent with the relative sulfur contents of the two coals (see Table 2).

TABLE 2. Physicochemical Properties of Two Coals Examined

		Utah coal	Illinois coal			Utah coal	Illinois coal
Moisture	wt. %	3.2	17.0	Si*	wt. %	1.225	1.820
Ash	wt. %	9.9 (10.2)	9.3 (11.2)	Al*	wt. %	0.738	0.823
Volatile	wt. %	42.0 (43.3)	33.9 (40.8)	S*	wt. %	0.527	4.165
Fixed C	wt. %	45.0 (46.4)	39.9 (48.0)	Ca*	wt. %	0.474	0.247
C	wt. %	71.51	59	Fe*	wt. %	0.238	1.093
H	wt. %	5.52	4.32	Na*	wt. %	0.203	0.110
N	wt. %	1.34	1.19	Mg*	wt. %	0.075	0.048
S	wt. %	0.37	3.11	K*	wt. %	0.051	0.115
O	wt. %	11.08	5.96	Cl*	wt. %	0.024	0.186
Cl	wt. %	0.03	0.17	P*	wt. %	0.005	ND
HHV	KJ/Kg	28,986	24,495	Zn*	wt. %	ND	0.003
Mean Dia.	µm	80	80	Mn*	wt. %	ND	0.003
				V*	wt. %	ND	0.002

Numbers in parentheses indicate wt. % dry basis; * XRF analysis; ND: Not detected

Figure 4: Exposure Chamber CEM Measurements and PM Concentrations during Utah Coal Ash Generation

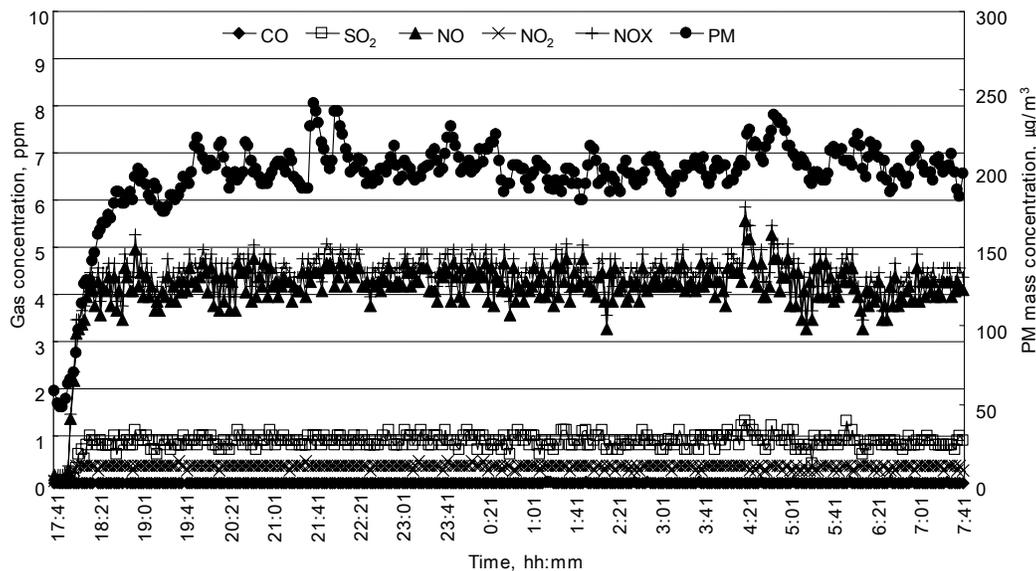


Figure 5: Submicron PSDs and particle Morphologies

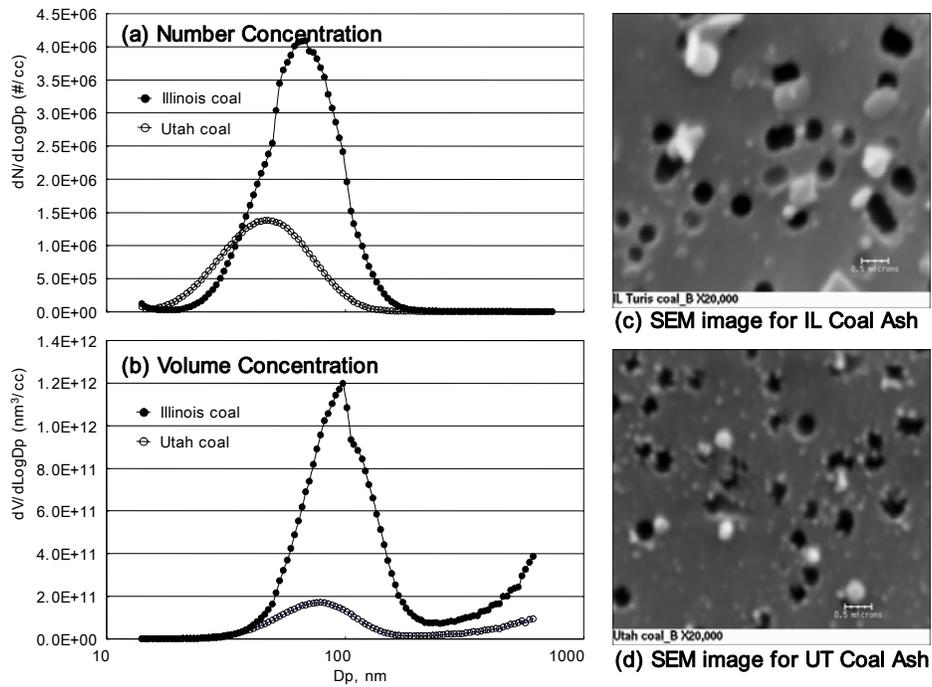


Figure 6: Results of XRF Analysis for Coal Ash Generation

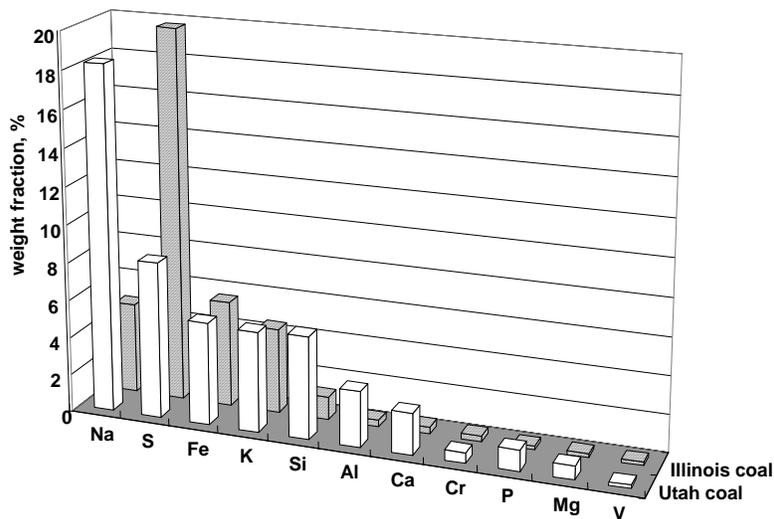
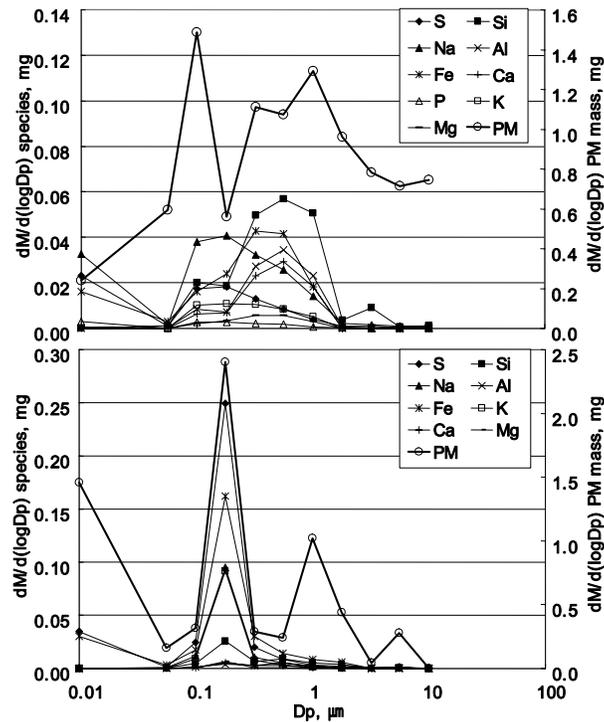


Figure 7 shows the distribution of species determined by XRF analysis of the MOUDI samples from the exposure chamber. In the case of Utah coal ash (Figure 7a), sodium is the

major constituent in the ultrafine mode ($\sim 0.1 \mu\text{m}$). In contrast, for the Illinois coal, sulfur and iron are the major constituents for of the ultrafine PM (Figure 7b). Differences in the mass concentrations and compositions of the ultrafine fractions of each coal are likely due to differences in the sulfur contents and ash species derived from sulfur and differences in the ash compositions of each coal. While fly ash composition is affected by coal type and ash constituents, comparison of the size dependent compositions of fly ash from the drop tube furnace and fly ash from a number of published laboratory-scale studies indicate similar elemental compositions and trends that the submicron aerosol is typically enriched in alkali and alkaline earth elements and sulfur, while the coarse mode fly ash is enriched in alumino-silicate species^{2,3,12,13,14}.

Figure 7: Results of XRF Analysis for MOUDI Sample from Coal Ash Generation



SUMMARY

This paper describes the design and characterization of an ultrafine coal ash generator that can be used for direct animal inhalation exposure studies. Operating parameters, including furnace temperature, coal feed rate, air flows, velocities, and residence time were considered. These are optimized such that the combustion and transport air flows and fuel feed match optimal flows through the cyclone system to produce reasonable submicron PM concentrations within the exposure chamber, as well as adequate relative humidity and minimal pressure drop.

Based on these optimized operating conditions, characterization experiments examined differences in the physical and chemical properties of the submicron fly ash from two coals.

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